Research Questions and Approach during Project

1) Does nucleation depend on the ionic ratio?
   - Measure time to form nuclei at different Ca:CO₃ ratios (DLS)
2) Are nuclei formed at high/low ionic ratio charged?
   - Measure nuclei charge vs. ionic ratio (Electrophoretic Light Scattering; ELS)
3) Does nucleus charge determine the critical nucleus size?
   - Measure nuclei size distributions during nucleation at different ionic ratio (DLS)
4) Does nucleus charge determine the ripening pathway?
   - Follow ripening of nuclei with time (morphology, crystallinity, transformation using liquid-cell and cryo-TEM)

Ultimate Goal of Project

- Derive new expressions to include nucleus charge in the nucleation thermodynamics, kinetics and ripening, by combining new relations with nucleation and colloid theories
- To apply the new theory on natural settings where expected crystal formation does not occur

Conclusions

- \( \text{CaCO}_3 \) nanoparticles nucleate and grow most rapidly at ideal \( \text{CaCO}_3 \) of 1
- In non-stoichiometric solutions, particle sizes remain < 10 nm up to a few hours
- The nucleation pathway is influenced by the ionic ratio of the solution

References


Figure 1: \( \text{BaSO}_4 \) scaling of geothermal energy, oil and gas pipelines leads to high repair and replacement costs.1

Figure 2: Importance of \( \text{CaCO}_3 \) scale formation in drinking water industries as it is a nuisance in industrial and household appliances.2

Figure 3: Experimental set-up during OLM-XPL experiments. The growth solutions (1); Peristaltic pump (2); Zen software for recording & imaging (3); Optical microscope (4); Axiocam attached to microscope (5); Beaker containing outflow solutions (6).3

Figure 4: DLS makes use of Brownian motion of nanoparticles in a solvent in order to measure their size distribution. Launching a laser into the particles and nanoparticle’s size distribution.4

Figure 5: Besides pH, ionic strength and the supersaturation degree (D), the ionic ratio affects the timing of nucleation (a) and how the newly formed particles grow at \( \text{CaCO}_3 \) of ~0.01, 1.0, 100 (b). Induction time measurements were obtained by Cross-Polarized Light Optical Microscopy (XPL-OLM) and the time represents nucleation and subsequent growth up to 20 μm (a). DLS (detection limit ± 0.3 nm) was used to investigate the growth of the crystals (b).5

Figure 6: two well known nucleation pathways: The classical nucleation pathway assuming ion-by-ion cluster formation and subsequent growth (upper) and the aggregation pathway, forming large postcritical nuclei from precluster-sized particles, followed by nucleation and subsequent growth (lower).6

Figure 7: Schematic representation of the reaction progress for the crystallization reaction in a pure system. It is a multistage crystallization pathway going from Amorphous Calcium Carbonate (ACC) → Vaterite → Calcite.7

Figure 8: {\textit{TEM}} images of ACC, vaterite, aragonite and calcite.8

Pilot Study: \( \text{CaCO}_3 \) nucleation and growth

Methods

Cross-Polarized Light in Optical Light Microscopy (XPL-OLM)

Dynamic Light Scattering (DLS)

Conclusions

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